Nucleation in binary polymer blends: Effects of foreign mesoscopic spherical particles

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We study nucleation in binary polymer blends in the presence of mesoscopic spherical particles using self-consistent field theory, considering both heterogeneous and homogeneous nucleation mechanisms. Heterogeneous nucleation is found to be highly sensitive to surface selectivity and particle size, with rather subtle dependence on the particle size. Particles that preferentially adsorb the nucleating species generally favor heterogeneous nucleation. For sufficiently strong adsorption, barrierless nucleation is possible. By comparing the free energy barrier for homogeneous and heterogeneous nucleation, we construct a kinetic phase diagram. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1761053]

I. INTRODUCTION

The dynamics of first-order phase transitions often involve heterogeneous nucleation owing to the ubiquitous existence of foreign particles that act as nucleation centers. For phase separation in polymer blends, small molecules (air, moisture), container wall, dust particles, or even polymers of different molecular weight can play the role of nucleation centers. The study of heterogeneous nucleation is thus of both theoretical interest and practical importance.

In comparison with homogeneous nucleation, heterogeneous nucleation exhibits several distinct features. Unlike homogeneous nucleation which is activated through random thermal fluctuations, heterogeneous nucleation always occurs at the location of the nucleating centers in a repeatable and deterministic manner. Another hallmark of the heterogeneous nucleation is the nearly monodisperse droplet distribution during the early stages of mechanism. Evidence of heterogeneous nucleation has been reported by Cumming *et al.* in binary polymer blends using light scattering technique.[1] In addition, for heterogeneous nucleation, there exists a threshold supersaturation beyond which nucleation becomes spontaneous (i.e., barrierless).[2]

In spite of its ubiquity and richness, there has been a dearth of experimental and theoretical work on heterogeneous nucleation; this is especially true for liquid-liquid phase separation in polymer blends. Existing heterogeneous nucleation theories are primarily concerned with gas to liquid transition.[2–8] Bykov and Zeng studied gas to liquid nucleation on mesoscopic particles by combining density functional theory (DFT) with classical nucleation theory.[2] Padilla and Talanquer investigated gas to liquid nucleation on aerosol particles[3] and Talanquer and Oxtoby examined gas to liquid nucleation on solid substrate,[4] both using DFT. DFT was also used to study the effect of the sign of charged particles in ion-induced nucleation of dipolar molecules.[5–8] To date, we are not aware of any theoretical work on heterogeneous nucleation in the liquid-liquid phase separation of polymer blends; the work presented here is an attempt at filling this gap.

Heterogeneous nucleation on particles is closely related to adsorption and wetting on foreign surfaces, which have been studied extensively with DFT,[5] the self-consistent field theory (SCFT) (Ref. 9) and computer simulations.[10] As in adsorption and wetting, heterogeneous nucleation on a particle surface depends on the surface property and its geometry.[5,7] In the case of polymer blends, depending on the particle size, we expect heterogeneous nucleation to take place in two ways: for mesoscopic spherical particles of sizes of the radius of gyration of the polymers or less, a spherical nucleus should form uniformly centered around the particles (complete wetting), while for larger particles, a more realistic scenario is to form a microlens shaped nucleus localized on the surface (partial wetting). In this study, we consider the first possibility.

For heterogeneous nucleation, the free energy barrier is the reversible work of formation of a critical nucleus from the metastable, fluid-solvated particle. The surface selective adsorption affects the free energy of both the metastable and critical nucleus. While the effects of surface selectivity on the metastable nucleus can be understood from studying the

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properties of equilibrium states, those on the critical nucleus cannot be deduced from the equilibrium properties. Direct theoretical studies are thus required to understand the effects of foreign particles on nucleation.

In this paper, we study heterogeneous nucleation in binary polymer blends in the presence of mesoscopic particles using the SCFT. For simplicity, the spherical particles are modeled as impenetrable hard spheres with specific surface selective interactions with the polymers. Our theoretical consideration of heterogenous nucleation is facilitated by the recent development of SCFT applied to homogeneous nucleation of polymer blends.[11–13] As demonstrated in Ref. 11, SCFT provides a unified description of nucleation at the mean-field level over the entire metastable region, particularly in the intermediate portion between the binodal and spinodal where neither Cahn-Hilliard theory[14–16] nor the classical theory[15,16] are reliable. Here we wish to understand how the surface selectivity and sizes of particles affect the heterogeneous nucleation and the competition between heterogeneous and homogeneous nucleation in blends containing mesoscopic particles.

The rest of this paper is organized as follows: In Sec. II, we briefly describe the SCFT of heterogeneous nucleation in polymer blends in the presence of spherical particles and the solution method for determining the metastable and the critical nucleus. The main results are presented and discussed in Sec. III. We first present the density profiles of the metastable and the critical nucleus, and then highlight the dependence of the free energy barrier for nucleation on the surface selectivity and sizes of particles, and finally, analyze the range of heterogeneous nucleation by comparing with homogeneous nucleation. The main findings and possible extensions are summarized in Sec. IV.

II. THEORY AND METHODOLOGY

A. Self-consistent field theory

We consider an incompressible binary polymer blend A/B around a mesoscopic spherical particle. The polymers are modeled as Gaussian chains of degrees of polymerization N_κ ($\kappa=A,B$) and for simplicity both A and B monomers are assumed to be of the same monomeric volume v and Kuhn length b. We choose units for the volume so that $v=1$. For studying nucleation in the metastable bulk phase, it is convenient to work in the grand canonical ensemble with chemical potentials μ_κ. Because the chemical potentials of the components in an incompressible mixture are not independent, we set $\mu_B=0$. The grand potential can be written as

$$\begin{aligned}\beta G[\phi_A,\phi_B,\omega_A,\omega_B,\xi] &= \int dr[\chi\phi_A(r)\phi_B(r)-H(r)\phi_A(r)+H(r)\phi_B(r)] \\ &\quad -\int dr\{\omega_A(r)\phi_A(r)+\omega_B(r)\phi_B(r) \\ &\quad -\xi(r)[\phi_A(r)+\phi_B(r)-1]\} \\ &\quad -\frac{\exp(\beta\mu_A N_A)}{N_A}Q_A[\omega_A]-\frac{1}{N_B}Q_B[\omega_B], \end{aligned} \tag{1}$$

where $\beta=1/(k_BT)$ and χ is Flory-Huggins interaction parameter. ϕ_κ is the volume fraction of monomer κ, ω_κ is the self-consistent molecular field conjugate to ϕ_κ, and ξ is an effective pressure field to ensure the local incompressibility of the binary blend. $H(r)$ is the interaction potential due to the spherical particle to be specified later.

In Eq. (1), Q_κ is the single chain partition function of chain κ in the presence of external field ω_κ:

$$Q_\kappa[\omega_\kappa]=\int dr q_\kappa(r,N_\kappa) \quad (\kappa=A,B), \tag{2}$$

where the end-segment distribution function $q_\kappa(r,N_\kappa)$ is obtained from solving the modified diffusion equation with the initial condition $q_\kappa(r,0)=1$,

$$\left[\frac{\partial}{\partial\tau}-\frac{b^2}{6}\nabla_r^2+\omega_\kappa(r)\right]q_\kappa(r,\tau)=0 \quad (\kappa=A,B). \tag{3}$$

The self-consistent field equations are obtained by a variational extremization of the grand potential with respect to ϕ_A, ϕ_B, ω_A, ω_B, ξ, respectively, which yields

$$\omega_A=\chi\phi_B-H+\xi, \tag{4}$$

$$\omega_B=\chi\phi_A+H+\xi, \tag{5}$$

$$\phi_A=\frac{\exp(\beta\mu_A N_A)}{N_A}\int_0^{N_A}d\tau q_A(r,\tau)q_A(r,N_A-\tau), \tag{6}$$

$$\phi_B=\frac{1}{N_B}\int_0^{N_B}d\tau q_B(r,\tau)q_B(r,N_B-\tau), \tag{7}$$

$$\phi_A+\phi_B=1. \tag{8}$$

By applying the self-consistent field equations to the homogeneous bulk state with volume fractions ϕ_A^0 and ϕ_B^0, the chemical potential of species A can be determined as

$$\beta\mu_A=\frac{1}{N_A}\ln\phi_A^0-\frac{1}{N_B}\ln\phi_B^0+\chi(1-2\phi_A^0). \tag{9}$$

With this expression for the chemical potential, the self-consistent field equation set can be solved to determine the metastable and critical nucleus. The free energy barrier for heterogeneous nucleation is defined as the work of formation of a critical nucleus from the metastable nucleus (i.e., the particle solvated by the metastable blend), that is, the free energy difference between the critical nucleus and the metastable nucleus,

$$\begin{aligned}\Delta F^*=G^*\{\phi_A^*,\phi_B^*,\omega_A^*,\omega_B^*,\xi^*\} \\ -G^m\{\phi_A^m,\phi_B^m,\omega_A^m,\omega_B^m,\xi^m\},\end{aligned} \tag{10}$$

where the superscripts $*$ and m denote the quantities of the critical nucleus and of the metastable nucleus, respectively. For simplicity of notation, we will omit the asterisk $*$ in the quantities for the critical nucleus. As a measure for the enhancement of the nucleating species, we follow Ref. 11 and define a material excess M^{ex} as $M^{ex}\equiv 4\pi\int_{r_p}^{\infty}r^2dr[\phi_A(r)-\phi_A^0]$, where r_p is the radius of the particle.

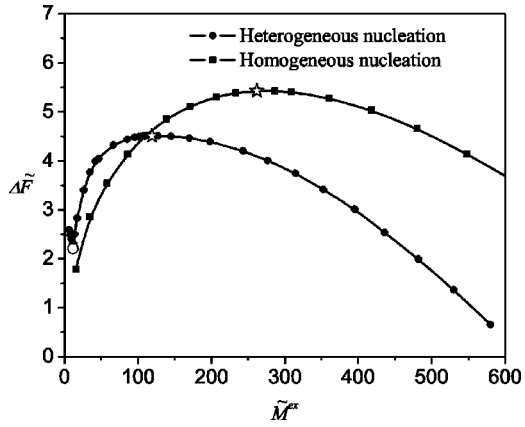

FIG. 1. Excess free energy as function of material excess for heterogeneous nucleation at $\phi_A^0=0.16$, $N\chi=2.5$, $\tilde{r}_p=2.5$, and $\Lambda=2.1$ (squares). The critical nucleus is marked by the star and the metastable nucleus is marked by the circle. The excess free energy for homogeneous nucleation at the same bulk condition is included for comparison (dots). For these parameters, heterogeneous nucleation requires a smaller barrier.

B. Method

For heterogeneous nucleation, both the metastable nucleus and the critical nucleus must be determined by solving the self-consistent field equations numerically. The metastable nucleus is obtained by a simple iterative scheme using the homogeneous bulk state as the initial solution. However, since the critical nucleus is the maximum of the free energy with respect to the material excess, the self-consistent field equations must be solved under the constraint of a specified material excess. For further details, we refer the readers to Ref. 11. Here we show in Fig. 1 a typical free energy surface along the material excess coordinate for heterogeneous nucleation ($N\chi=2.5$, $\tilde{r}_p=2.5$, and $\Lambda=2.1$; dimensionless quantities introduced in Sec. III are used). The critical nucleus is identified with the maximum and the metastable nucleus is identified with the minimum. For comparison, we also include the free energy surface for homogeneous nucleation at the same bulk condition.

The particle is modeled as an impenetrable spherical particle of radius r_p with surface interaction $H(r)$ with polymers. For a blend of components of the same molecular weight we consider in this paper, the total density fluctuation very near the surface is negligible. Therefore, we adopt the reflective boundary condition on the particle surface.[17] We choose a short-ranged surface potential of the form $H(r)=\Lambda h(r)$, where Λ is the strength of the potential, and $h(r)$ is defined such that, if $r_p\leqslant r\leqslant r_p+r_c$ where r_c is some cutoff distance from the surface of the sphere, $h(r)=1$; otherwise, $h(r)=0$. In our calculation, we set $r_c=(1/30)N^{1/2}b$. Note that the particle attracts component A if Λ is positive and repels A if Λ is negative. Because of the incompressibility, attraction of one of the polymer species means repulsion of the other.

III. RESULTS AND DISCUSSION

In order to focus on the effects of the particle, we take both polymer species to be of the same degree of polymerization, that is, $N_A=N_B=N$. To make the results applicable to general N, we characterize the incompatibility of the two polymer species by $N\chi$ and introduce the following dimensionless properties: $\tilde{r}\equiv r(N^{1/2}b)$, $\tilde{M}^{ex}\equiv M^{ex}(N^{3/2}b^3)$, $\tilde{G}\equiv\beta G v(N^{1/2}v/b^3)$, and $\Delta\tilde{F}\equiv\beta\Delta F v(N^{1/2}v/b^3)$.

Heterogeneous nucleation on mesoscopic spherical particles shares some common characteristics with homogeneous nucleation. For homogeneous nucleation, as the blend immiscibility increases from the coexistence to the spinodal, the critical nucleus crosses over from a nearly uniform core with a well-defined interface to a diffusive profile, and the free energy barrier for nucleation decreases monotonously from the coexistence where it diverges to the spinodal where it vanishes. Heterogenous nucleation exhibits similar qualitative behavior upon varying the immiscibility. However, the existence of the foreign particle gives rise to some new features.

In the following discussion, we first present the density profiles of the metastable and critical nucleus, and then discuss the dependence of the free energy barrier for heterogeneous nucleation on the surface selective potential and particle size in connection with the density profiles, and lastly, examine the competition between heterogeneous and homogeneous nucleation. Only the results with $\phi_A^0=0.16$ are presented here; thus A is the nucleating species. No new qualitative effects are expected by changing ϕ_A^0. At $\phi_A^0=0.16$, the metastable region is bounded by $(N\chi)_{coex}=2.44$ at the coexistence curve and $(N\chi)_s=3.72$ at the spinodal. The complete phase diagram is given in Ref. 11 and will not be reproduced here. On physical grounds, we expect that heterogeneous nucleation is favored over homogeneous nucleation only when the particle attracts the nucleating species, i.e., $\Lambda>0$. ($\Lambda>0$ is a necessary but not a sufficient condition to favor heterogeneous nucleation; see Sec. III C.) However, for completeness and also for comparison, we include results for $\Lambda<0$ as well.

A. Density profiles of critical nucleus and metastable nucleus

The density profiles of the critical nucleus and the metastable nucleus at different conditions are compared in Figs. 2 and 3. Figures 2(a)–2(c) show the comparison of density profiles at different surface potentials and fixed particle size and immiscibility, Figs. 2(d)–2(f) show the density profile comparison among different values of immiscibility at fixed particle size and surface potential, and the comparison of density profiles at different particle sizes and fixed surface potential and immiscibility is shown in Figs. 3(a) and 3(b).

Whereas in the case of homogeneous nucleation the metastable state is the uniform bulk state, for heterogeneous nucleation around a particle, the metastable state, referred to as the metastable nucleus in this paper, corresponds to the particle solvated by the blend medium. The metastable nucleus is a local minimum in the free energy and its properties can be justified on the grounds of equilibrium considerations. In the metastable nucleus, one species is enriched around the particle surface due to the surface selective interaction at the expense of the translational entropy of the adsorbed species, with an attended increase (decrease) in the enthalpic contribution [the first term in Eq. (1)] near the sur-

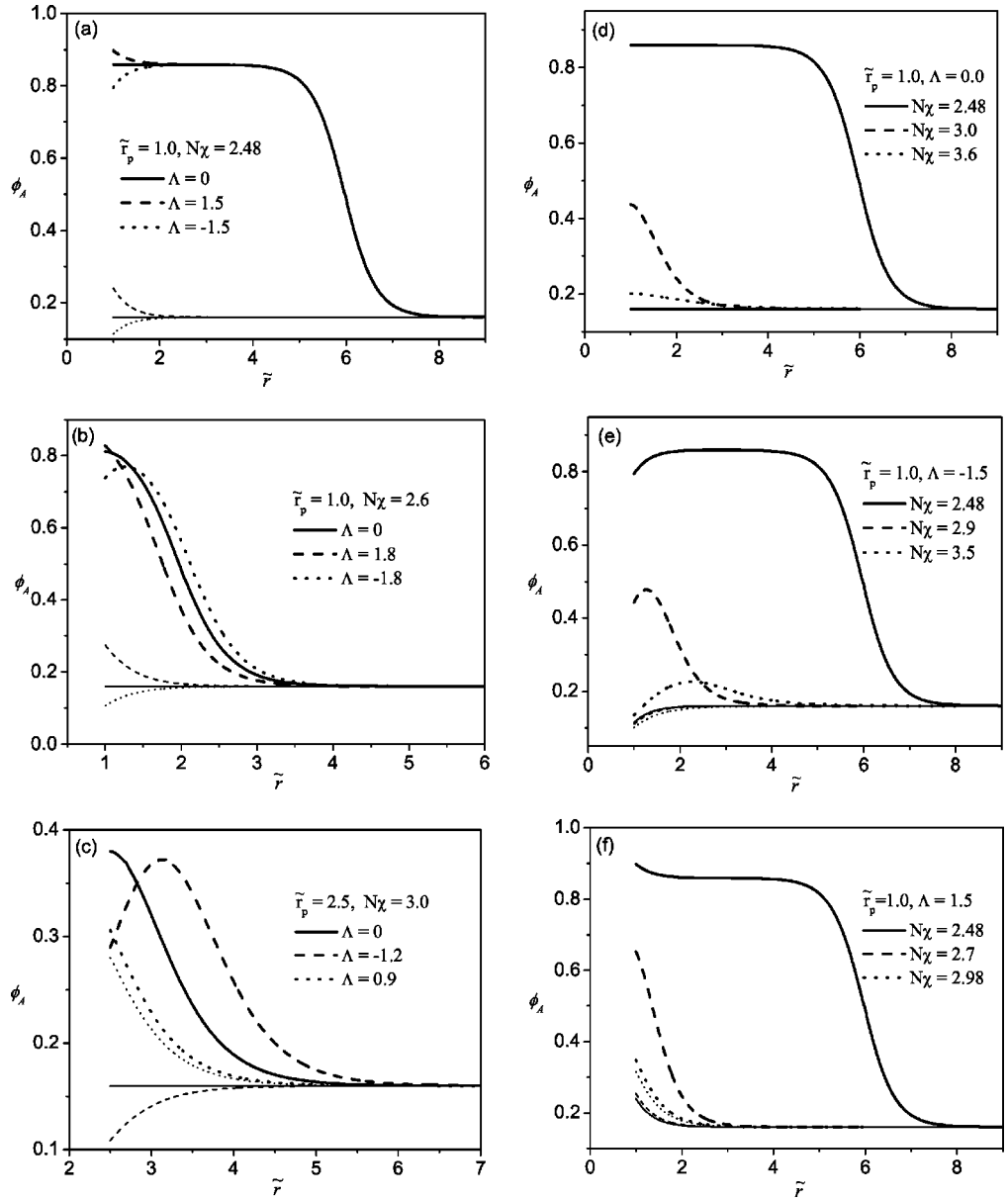

FIG. 2. Representative density profiles of critical nucleus and its corresponding metastable nucleus at $\phi_A^0 = 0.16$. The thick lines correspond to the critical nucleus, while the thin lines are for the metastable nucleus. Distance is normalized by $N^{1/2}b$. (a)–(c) Variation of the density profiles with the surface potential; (d)–(e) variation of the density profiles with the immiscibility.

face if the surface absorbs the minor (major) species. Thus the metastable nucleus exhibits monotonic density variation along the radial direction in Figs. 2 and 3.

The general feature to be observed in Figs. 2(a)–2(c) is that for given a particle size and blend immiscibility, the metastable nucleus with $\Lambda > 0$ always exhibits larger adsorption than that with $\Lambda < 0$ for the same magnitude of Λ. This is a result from the composition asymmetry: since the major

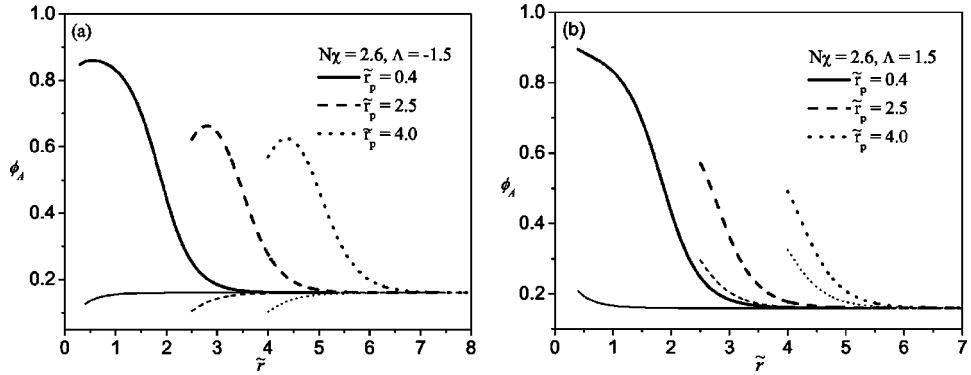

FIG. 3. Representative density profiles of critical nucleus and its corresponding metastable nucleus at different particle sizes and $\phi_A^0 = 0.16$. The thick lines correspond to the critical nucleus, while the thin lines are for the metastable nucleus. Distance is normalized by $N^{1/2}b$. (a) Surface potential $\Lambda = -1.5$; (b) surface potential $\Lambda = 1.5$.

species already has a larger concentration around the sphere, the same additional attraction by the sphere will lead to less of an increase in its density than if the adsorbed species is the minor, nucleating species. In both cases, the content (in the sense of the material excess) of metastable nucleus grows with increasing $|\Lambda|$, although the length scale is primarily determined by the bulk correlation length of the blend.

Larger immiscibility, which corresponds to longer correlation length, leads to larger metastable nucleus, as shown in Figs. 2(d)–2(f). The metastable nucleus also grows with increasing particle size due to the increased surface interaction, as can be seen from Figs. 3(a) and 3(b).

In contrast to the metastable nucleus, features of the critical nucleus are somewhat subtle and nonintuitive. The way surface selectivity affects the density profiles of the critical nucleus depends on the immiscibility. Near the binodal, homogeneous nucleation involves dropletlike critical nuclei with sharp interfaces and nearly uniform concentration inside the nuclei. In the case of heterogeneous nucleation around particles near the coexistence, selective adsorption by the particle surface perturbs the uniform distribution of the nucleating species and an additional interfacial layer forms next to the particles surface inside the critical nucleus as shown in Fig. 2(a). Depending on the sign of Λ, the nucleating species can either show enrichment (for $\Lambda>0$) or depletion (for $\Lambda<0$) near the particle surface. As we march from the coexistence toward the spinodal, a diffusive and monotonically decaying density profile of the critical nucleus is expected for homogeneous nucleation. However, as shown in Figs. 2(b) and 2(c), heterogeneous nucleation on a particle that preferentially adsorbs the *B* species requires the formation of a depletion layer of the nucleating *A* species; nucleation occurs outside of this depletion layer much like homogeneous nucleation in the bulk phase. More interestingly, heterogeneous nucleation on a particle that prefers the nucleating *A* species requires lower enrichment of the *A* species, since the particle has the effect of cutting off the density profile at $r=r_p$.

Upon close examination of the density profiles of the critical nuclei, we can see that increasing the particle size has similar qualitative effects to increasing the blend immiscibility. Very near the coexistence, the critical nucleus of homogeneous nucleation is much larger than the particles, and therefore the presence of the particle has little effect on the interface of critical nucleus; only the region very near the surface is affected. Departing from the coexistence, the core of critical nucleus of homogeneous nucleation decreases, and when its size becomes comparable to the particle size, the interface is perturbed, leading to a decrease in the enrichment of the nucleating species. These features are shown in Fig. 3. Increasing the size of the particle to around the size of the critical nucleus of homogeneous nucleation or larger results in a significant interruption of the interface of critical nucleus and consequently a decease in the density of the nucleating species on the particle surface. This behavior helps explain the decrease in the free energy of critical nucleus, as will be discussed further in the following.

Thus, in contrast to the metastable nucleus, the critical nucleus with $\Lambda>0$ is always smaller than that with $\Lambda<0$ when the blend is well beyond the coexistence boundary, the difference increasing with increasing $|\Lambda|$. As shown in Fig. 2(c), when $|\Lambda|$ increases, the critical nucleus shrinks for $\Lambda>0$ and grows for $\Lambda<0$.

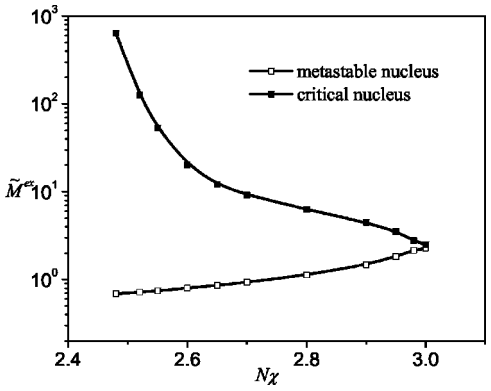

FIG. 4. Dependence of the material excess of critical nucleus and metastable nucleus on the blend immiscibility at $\Lambda=1.5$, $\tilde{r}_p=1.0$, and $\phi_A^0=0.16$.

Because the size of the critical nucleus decreases and that of the metastable nucleus increases with Λ, for large and positive Λ, the two approach each other, and coincide at some point. At this point, the free energy barrier for heterogeneous nucleation vanishes. However, the material excess remains finite, as shown in Fig. 4. Barrierless heterogeneous nucleation can also be achieved by increasing the particle sizes and/or the blend immiscibility.

B. Free energy barrier for heterogeneous nucleation

The presence of foreign particles affects the free energy barrier for heterogeneous nucleation through volume exclusion, selective surface adsorption, and a concomitant change in the enthalpic part of the free energy. We first discuss the effects of the surface selectivity at fixed particle size and blend immiscibility and then discuss the effects of the particle size.

The free energy barrier for nucleation on spherical particles decreases monotonically with increasing adsorption of the nucleating species. Figure 5 shows the order in the free

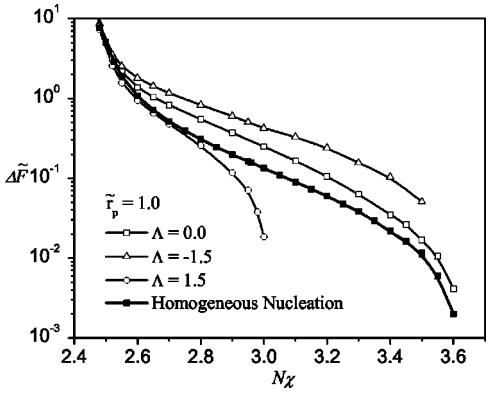

FIG. 5. Comparison of the free energy barrier as function of the immiscibility at $\phi_A^0=0.16$ between homogeneous nucleation and heterogenous nucleation on particles of $\tilde{r}_p=1.0$ with several values of the surface potentials.

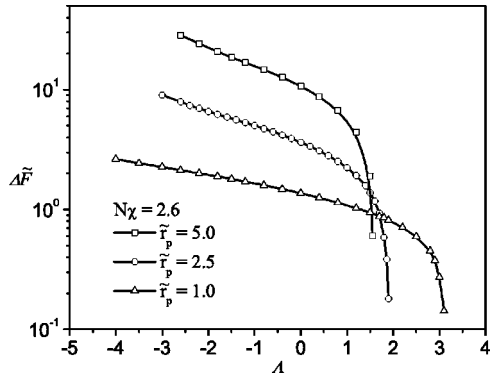

FIG. 6. Dependence of the free energy barrier for nucleation on the surface potential at different particle sizes and $\phi_A^0 = 0.16$.

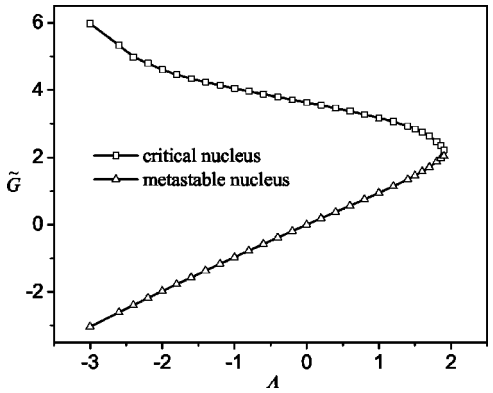

FIG. 8. Dependence of the grand potentials of critical nucleus and metastable nucleus on the surface potential at $N\chi = 2.6$, $\tilde{r}_p = 2.5$, and $\phi_A^0 = 0.16$. The grand potentials are calculated using the homogeneous bulk as reference.

energy barrier for heterogeneous nucleation on particles of the same size ($\tilde{r}_p = 1.0$) at the same immiscibility: particles adsorbing the nucleating component ($\Lambda = 1.5$) < neutral particles ($\Lambda = 0$) < particles adsorbing the major component ($\Lambda = -1.5$). If the sizes of particles and the immiscibility are fixed, the free energy barrier for heterogeneous nucleation decreases monotonically with Λ as shown in Figs. 6 and 7 and drops precipitously when Λ reaches some value, after which point barrierless nucleation occurs. The latter is corroborated by the overlap of the metastable nucleus and the critical nucleus at the same value of Λ. Figure 6 shows that the threshold surface potential to achieve barrierless nucleation decreases with increasing the sizes of particles. Similarly, Fig. 7 shows that increasing the immiscibility decreases the threshold value.

The dependence of the free energy barrier on the surface potential results from a combination of two effects: the free energy of the metastable nucleus increases with Λ while the free energy of the critical nucleus decreases with Λ, as shown in Fig. 8. The free energies of the metastable nucleus and the critical nucleus are identified, respectively, from the local minimum and maximum of the free energy curve along the material excess coordinate as illustrated in Fig. 1. The monotonic increase of the free energy of the metastable nucleus can be understood by a simple random mixing argument. Assuming no change in the density profile of the components, the interaction of the blend with the surface has the form of $(4\pi/3)\Lambda[(\tilde{r}_p + \tilde{r}_c)^3 - \tilde{r}_p^3](\phi_B - \phi_A)$ [cf. Eq. (1)], which justifies the nearly straight line behavior of $\tilde{G}$ with Λ as well as the change in sign at $\Lambda = 0$. More rigorously, however, the monotonic increase in the free energy for the metastable nucleus results from a combination of surface adsorption, spatial inhomogeneity, and the concomitant change in the enthalpic term $\chi\phi_A\phi_B$. The explanation of the monotonic decrease of the free energy of the critical nucleus with Λ is less straightforward. However, since the density of the nucleating species A is higher than that of major bulk component B inside the critical nucleus, heuristically we expect the free energy to decrease if the particle adsorbs the nucleating species A and to increase if the particle adsorbs B.

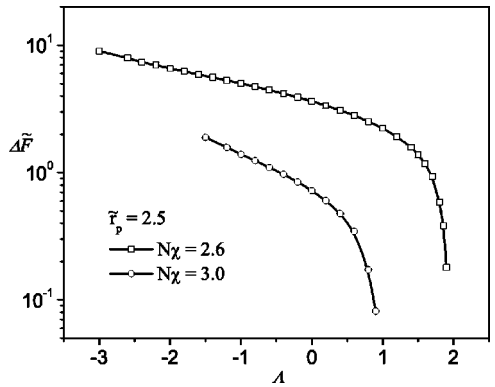

FIG. 7. Dependence of the free energy barrier for nucleation on the surface potential at different values of immiscibility and $\phi_A^0 = 0.16$.

For sufficiently large and positive Λ, i.e., when the particle adsorbs the nucleating species sufficiently strongly, nucleation can become barrierless. As mentioned above, upon increasing the surface potential Λ selective to the nucleating species A, the metastable nucleus grows and the critical nucleus shrinks, and they approach each other. At a threshold value of Λ, the metastable nucleus and the critical nucleus become identical; phase separation thus occurs spontaneously without any free energy barrier. Note that such barrierless nucleation is different from spinodal decomposition or homogeneous nucleation at the bulk spinodal. In the latter cases, the blend is unstable with respect to infinitesimal fluctuation, whereas for barrierless heterogeneous nucleation, the bulk blend is stable against small thermal fluctuations, and phase separation starts from the local, large concentration fluctuation induced by the strong selective adsorption by the particle. The mechanism takes on a distinct nucleation-and-growth feature character and is associated with a finite material excess as shown in Fig. 4. The concentration fluctuation develops and grows radially around the nucleation center, i.e., the particle, until it is interrupted by concentration fluctuation from another nucleus. Although barrierless nucleation has been discussed in the gas to liquid transition,[2] the mechanism has not received much attention in the phase separation of polymer blends. When conditions are met for barriarless nucleation to occur, homogeneous nucleation becomes irrelevant, and phase separation will follow a heterogeneous mechanism. The uniformly dispersed spherical

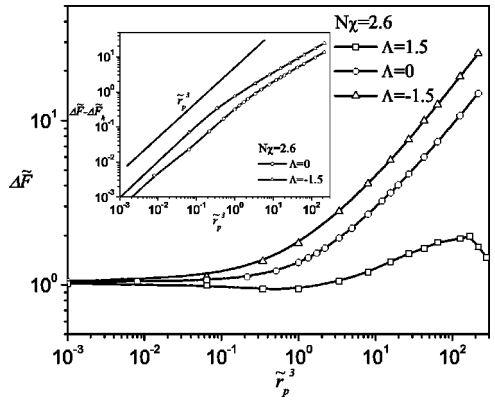

FIG. 9. Dependence of the difference of free energy barriers between heterogeneous and homogeneous nucleation on the cube of particle size $\tilde{r}_p^3$ at different values of surface potential, $N\chi=2.6$ and $\phi_A^0=0.16$. $\Delta\tilde{F}_h$ is the free energy barrier for homogeneous nucleation at the same conditions.

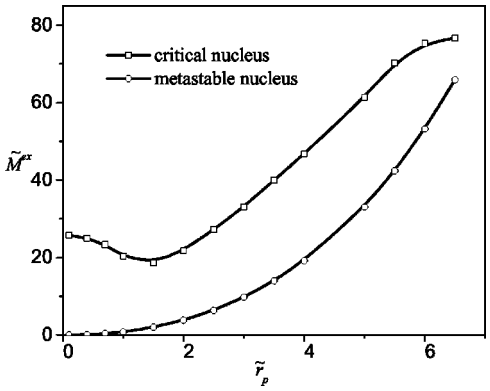

FIG. 10. Dependence of the material excess of the critical nucleus and that of the metastable nucleus for nucleation on the particle size at $\Lambda=1.5$, $N\chi=2.6$, and $\phi_A^0=0.16$.

droplets observed at early stage of phase separation in Ref. 1 may well be a manifestation of barrierless or nearly barrierless nucleation.

We now discuss the effects of particle size. An obvious effect due to the presence of the particle is volume exclusion inside the nucleus, whose influence on the free energy barrier for nucleation can be understood readily in the framework of the classical nucleation theory.[5,6,18,19] In the classical theory, the free energy of the nucleus consists of a negative bulk term and a positive interfacial term, and the critical nucleus is determined by maximizing the free energy. In the absence of selective surface adsorption, the free energy of a nucleating droplet around a spherical particle can be written as

$$\Delta F=4\pi(R^3-r_p^3)(g-g_0)/3+4\pi R^2\gamma, \tag{11}$$

where γ is the interfacial tension, g is grand potential density of the incipient phase. The critical nucleus is determined by the condition $\partial\Delta F/\partial R=0$, which yields

$$R=2\gamma/(g_0-g). \tag{12}$$

Thus, the presence of a particle in the center of the nucleus has no effect on the radius of critical nucleus, but decreases the magnitude of the negative bulk term by an amount proportional to the volume of the particle just as indicated in Eq. (11). This shifts the free energy upwards by a constant amount $-4\pi r_p^3(g-g_0)/3$. When this effect is combined with selective surface adsorption of the nucleating species, the resulting dependence of the free energy barrier on the particle size can be subtle and complicated. Below we examine the particle size effects at fixed surface potential and blend immiscibility.

First we consider the case of neutral particles and particles adsorbing the major species. For neutral particles, as shown in Fig. 9, the free energy barrier increases monotonically with increasing neutral particle sizes, reflecting the $\tilde{r}_p^3$ dependence of the volume exclusion effect alluded to above; see the inset in this figure. Particles adsorbing the major species show similar dependence. The free energy increase is even larger compared to the neutral case because of the additional surface selective adsorption of the non-nucleating species. Note that for large particle sizes, the presence of the particle interferes with the concentration profiles of the critical nucleus to the extent that the density of the nucleating species on particle surface decreases, as shown in Fig. 3(a), which has the tendency to decrease the free energy of the critical nucleus. As a result, the barrier increase with particle size slows down at large particle sizes.

When the particles adsorb the nucleating A species, the free energy barrier exhibits nonmonotonic dependence on the particle size. Figure 9 shows that at a fixed immiscibility, the free energy barrier first decreases slightly, then increases and then decreases again, as the particle size increases. Such a behavior reflects the subtle competition between volume exclusion and selective surface adsorption, both increasing with the particle size but with opposing effects. For the metastable nucleus, the material excess increases monotonically with increasing particle sizes as shown in Fig. 10, and its free energy increases correspondingly (not shown here) because of the dominant enthalpic contribution from $\chi\int dr\,\phi_A(r)\phi_B(r)$. In contrast, the effect of particle size on the critical nucleus is complicated. When particles are small relative to the critical nucleus of homogeneous nucleation under the same conditions, the nucleating species is enriched near the particle surface, and increasing the particle size decreases the material excess of the nucleating species as shown in Fig. 10. This leads to a decrease in the free energy barrier for heterogeneous nucleation. Upon further increasing the particle size, however, although the density of the nucleating species on particle surface decreases, overall the material excess still increases, which in turn increase the free energy of the critical nucleus. Since the increase of the material excess for the critical nucleus is larger than that for the metastable nucleus, the free energy barrier for nucleation increases. However, when the particle size is large enough as to interrupt the interface of critical nucleus of homogeneous nucleation under the same conditions, the decrease of the density of the nucleating species on particle surface becomes significant. At the same time since the increase of the material excess for the critical nucleus is less than that for the metastable nucleus, the free energy barrier decreases again. As we increase the blend immiscibility from the coexistence towards the spinodal, the metastable nucleus grows due to increased correlation length as mentioned before. On the

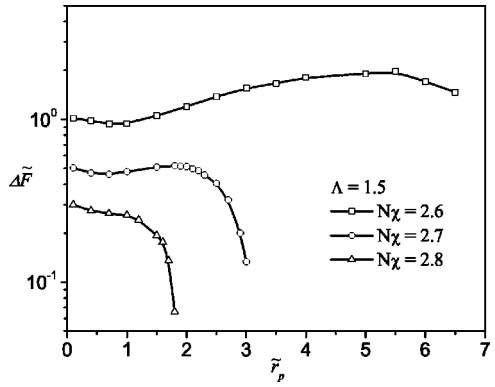

FIG. 11. Dependence of the free energy barrier for nucleation on the particle size at different values of immiscibility, $\Lambda = 1.5$ and $\phi_A^0 = 0.16$.

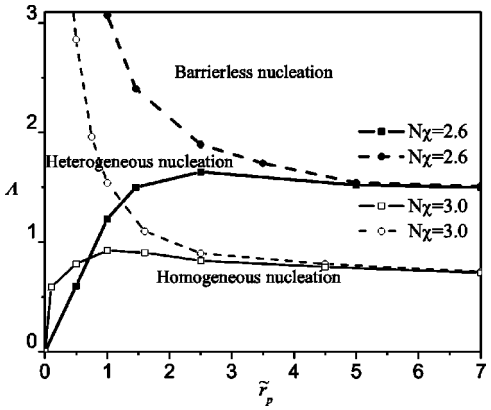

FIG. 12. Representative kinetic phase diagram showing the boundaries between regions of homogenous nucleation, heterogeneous nucleation, and barrierless nucleation. The square-marked lines denote the boundary between homogeneous and heterogeneous nucleation, and the circle-marked lines denote the boundary for barrierless nucleation.

other hand, the critical nucleus of homogeneous nucleation shrinks near the coexistence, and grows but become very diffusive near the spinodal, whose interface can be interrupted by smaller particles. Thus the aforementioned behavior takes place at smaller particle sizes, as shown in Fig. 11. For sufficiently large immiscibility, the free energy barrier becomes a rapidly decreasing, monotonic function. When the particle adsorbs the nucleating species, it is possible to achieve barrierless nucleation by increasing the blend immiscibility and/or particle size.

The competition between volume exclusion, surface selective adsorption, and the concomitant change in the enthalpic part of the free energy is also manifested in Fig. 6. Although at negative or small positive values of Λ the free energy barrier increases with particle size, the trend is quickly reversed at larger values of Λ. This suggests that the volume exclusion and surface selective adsorption have the same effects for $\Lambda < 0$, the volume exclusion dominates for low $\Lambda > 0$, and the surface adsorption and the concomitant change of the enthalpic part of the free energy dominate for larger $\Lambda > 0$, the effects being enhanced in the last case with increasing the particle size.

C. Competition between heterogeneous nucleation and homogeneous nucleation

In the presence of foreign mesoscopic particles, whether nucleation occurs through the homogeneous or heterogeneous mechanism depends on the rates of these mechanisms; the one with the larger rate is the dominant mechanism. Assuming an Arrhenius relationship[20] between the nucleation rate and the free energy barrier and neglecting the preexponential kinetic factor, we can compare the nucleation rate by comparing the free energy barrier for nucleation. Many factors including the local density profiles due to preferential adsorption can have effects on the nucleation rate through the preexponent factor. However, the determination of these effects is a kinetic issue that is beyond the scope of this paper. Since our interest here is not to determine the rate per se but the dominant nucleation mechanism, and the free energy barrier enters in the exponential of the rate expression, as a first approximation, it is reasonable to compare just the free energy barrier for the different mechanisms.

In a binary polymer blend containing mesoscopic particles, phase separation in the metastable region can occur through homogeneous nucleation, heterogeneous nucleation, or barrierless nucleation. Figure 12 shows a representative kinetic phase diagram which delineates the boundaries between the different nucleation mechanisms. When the particle adsorbs the major component or is nonselective (i.e., $\Lambda \leqslant 0$), homogeneous nucleation dominates regardless of particle size. This dominance persists even for particles that slightly attract the nucleating species because of the dominant volume exclusion effect. For larger $\Lambda > 0$, the barrier for heterogeneous nucleation decreases relative to that for the homogeneous nucleation, and when Λ is sufficiently large, heterogeneous nucleation becomes favored over homogeneous nucleation. Small-sized particles are more effective in inducing heterogeneous nucleation, as clearly seen in the figure. As the particle size increases, stronger attraction of the nucleating species (i.e., larger Λ) is required for the changeover from homogeneous to heterogeneous nucleation mechanism. For even larger particle sizes, the heterogeneous/homogeneous boundary decreases (though only slightly) again. In the region where heterogeneous nucleation is favored, for sufficiently large Λ, increasing the particle size and/or surface selective potential decreases the free energy barrier, eventually leading to barrierless nucleation. Note that for large particle sizes, the region for heterogeneous nucleation with a finite nucleation barrier is quite narrow and shrinks further with increasing particle sizes; this reflects the rapid decrease of the free energy barrier with the increasing strength of adsorption for the nucleation component at large particle sizes.

The qualitative features of the kinetic phase diagram is consistent with our discussion of the free energy barrier. For example, the nonmonotonic boundary between homogeneous and heterogeneous nucleation reflects the competition between surface selective adsorption and volume exclusion. When the particles are much smaller than the critical nucleus for homogeneous nucleation, surface adsorption dominates over volume exclusion in the free energy barrier. Upon increasing the particle size, the surface selective potential at

the homogeneous/heterogeneous boundary needs to increase to off-set the increased volume exclusion effect. When the particles are sufficiently large as to interrupt the profile of the critical nucleus for homogeneous nucleation, the reduction in the material excess of the critical nucleus relative to that of the metastable nucleus, and hence the excess free energy for the formation of the critical nucleus, become significant. Thus slightly smaller values of the surface selective potential are required for the system to switch from homogeneous to heterogeneous nucleation mechanism. A similar, though more pronounced effect accounts for the decrease of the surface selective potential with the particle size on the line for barrierless transition.

The gross topology of the kinetic phase diagram remains unchanged when changing the immiscibility. However, as expected, for larger immiscibility the boundary between homogeneous and heterogeneous nucleation as well as the line for barrierless nucleation both shift to smaller values of Λ, reflecting that a weaker external perturbation is required to induce the concentration fluctuation that leads to phase separation.

IV. CONCLUSION

Using the self-consistent-field method, we have studied nucleation in a binary polymer blend when foreign, mesoscopic particles are present, with a focus on the effects of surface selectivity and particle size. For neutral particles and particles adsorbing the major component, homogeneous nucleation prevails regardless of the particle size. In the case of particles adsorbing the nucleating species, strong adsorption makes heterogeneous nucleation favored over homogeneous nucleation, with a nonmonotonic dependence on the particle size. For sufficiently strong adsorption strength or large particle size, heterogeneous nucleation can become barrierless. Our study thus provides, at the mean-field level, a complete description of the kinetic scenarios for phase separation in a binary polymer blend containing mesoscopic particles.

In this paper, we have assumed that the particles are small enough so that heterogeneous nucleation occurs around the particle radially. For larger particles or less curved surfaces, such as the container wall, formation of microlens-shaped critical nuclei is more likely. We hope to extend our method to these cases.

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[1] A. Cumming, P. Wiltzius, F. S. Bates, and J. H. Rosedale, Phys. Rev. A **45**, 885 (1992).
[2] T. V. Bykov and X. C. Zeng, J. Chem. Phys. **117**, 1851 (2002).
[3] K. Padilla and V. Talanquer, J. Chem. Phys. **114**, 1319 (2001).
[4] V. Talanquer and D. W. Oxtoby, J. Chem. Phys. **104**, 1483 (1996).
[5] V. Talanquer and D. W. Oxtoby, Physica A **220**, 74 (1995).
[6] V. Talanquer and D. W. Oxtoby, J. Chem. Phys. **103**, 3686 (1995).
[7] I. Kusaka, Z.-G. Wang, and J. H. Seinfeld, J. Chem. Phys. **102**, 913 (1995).
[8] I. Kusaka, Z.-G. Wang, and J. H. Seinfeld, J. Chem. Phys. **103**, 8993 (1995).
[9] M. Muller, E. V. Albano, and K. Binder, Phys. Rev. E **62**, 5281 (2000).
[10] M. Muller, Comput. Phys. Commun. **147**, 292 (2002).
[11] S. M. Wood and Z.-G. Wang, J. Chem. Phys. **116**, 2289 (2002).
[12] J. F. Wang, H. D. Zhang, F. Qiu, Z.-G. Wang, and Y. L. Yang, J. Chem. Phys. **118**, 8997 (2003).
[13] M. Muller, L. G. Macdowell, P. Virnau, and K. Binder, J. Chem. Phys. **117**, 5480 (2002).
[14] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **31**, 688 (1959).
[15] K. Binder, J. Chem. Phys. **79**, 6387 (1983).
[16] K. Binder, Phys. Rev. A **29**, 341 (1984).
[17] D. T. Wu and G. H. Fredrickson, J. Chem. Phys. **104**, 6387 (1996).
[18] M. Volmer, *Kinetik der Phasenbildung* (Steinkopff, Dresden, 1939).
[19] D. Turnbull, J. Chem. Phys. **18**, 198 (1950).
[20] R. H. Doremus, *Rates of Phase Transformation* (Academic, New York, 1985).